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This research program has produced experimentally the phase diagrams of In-Ga-As, In-Ga-P and In-As-P ternary alloys for the first time over their entire composition range using liquid phase epitaxy techniques. A thermodynamical model based on the simple solution model was developed and more accurate values for several thermodynamical parameters based on extended solidus data for these ternary compounds were obtained. Also a model has been presented to account for the so-called lattice-pulling effect and has been successfully applied to the InGaP/GaAs system. Electrical and structural properties of the epitaxial layers have been studied. The Epitaxial growth of →

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PHASE DIAGRAM OF III-V COMPOUNDS BY THE STEP GRADING TECHNIQUE

Final Report

(December 1978 - September 1982)

by

S.M. Bedair, C. Morrison and J.R. Hauser
Department of Electrical Engineering
N. C. State University
Raleigh, NC 27650

Sponsored by

U.S. Army Office of Research
Research Triangle Park, NC 27709

ABSTRACT

This research program has produced experimentally the phase diagrams of In-Ga-As, In-Ga-P and In-As-P ternary alloys for the first time over their entire composition range using liquid phase epitaxy techniques. A thermodynamical model based on the simple solution model was developed and more accurate values for several thermodynamical parameters based on extended solidus data for these ternary compounds were obtained. Also a model has been presented to account for the so-called lattice-pulling effect and has been successfully applied to the InGaP/GaAs system. Electrical and structural properties of the epitaxial layers have been studied. The Epitaxial growth of these ternaries both on GaAs and InP substrates assisted in the development of two devices: the cascade solar cell and a photodetector for the 1.8 to 2.0 μm range.

Finally, this program has contributed to the development of the solid state laboratories in the Department of Electrical Engineering at North Carolina State University and has supported research incorporated in a Ph.D. thesis and several published papers.

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I. PHASE DIAGRAMS

The main thrust of the research program has been the development of the phase diagrams of In-Ga-As, In-Ga-P, and In-As-P over their entire composition range for select temperatures using liquid phase epitaxy (LPE) techniques. These ternaries, besides their importance in their own right, serve as three of the four boundaries of the quaternary InGaAsP which has attracted considerable attention lately. Due to the presence of lattice parameter mismatch between these ternary alloys and their end binary compounds, solidus data obtained by growing only one epitaxial layer has been available only near the corners of the compositional plane. The use of this limited information to deduce several thermodynamic parameters that are needed for the theoretical prediction of the phase diagrams resulted in contradictory values being reported for these parameters. It was realized that the lack of accurate values for these ternary parameters is one of the main reasons for the disagreements between experimental and theoretical results for the ternary systems and also of the InGaAsP quaternary.

(A) In-Ga-As

Rather than trying to grow one layer epitaxially on a binary substrate, stepwise compositional grading layers can be grown instead. The alloy composition and hence the lattice parameters can be changed from the substrate to any desired value in small, but abrupt increments. Thus the effect of lattice mismatch between the substrate and the first ternary layer and between the successive layers can be reduced to allow successful stepwise growth. This technique has been successfully applied in our laboratory to the $In_xGa_{1-x}As$ system to obtain solidus isotherms up to $x \approx 0.64$, through seven successive epitaxial layers on a GaAs substrate. This is a much larger "x" value than any published data for this ternary of which we are aware. Previous values for $In_xGa_{1-x}As$ layers on GaAs were only in the range of $x < 0.2$.

Liquidus and solidus data were developed for the 650,700, and 800°C isotherms in the In-rich corner of the Ga-In-As ternary system. LPE has been used to grow eight successive step layers of $Ga_{1-x}In_xAs$ on GaAs substrate material, and each one of these layers provides a solidus data point for this ternary. The present technique predicts the conditions for successful lattice-matched growth of $In_xGa_{1-x}As$ on InP substrates. The accurate knowledge of the solidus and liquidus isotherms resulted in epitaxial growth of $In_xGa_{1-x}As(0 < x < 0.3)$ with quality better than that previously obtained by VPE and LPE techniques. The simple solution model, successfully applied before for limited solidus data, does not seem to be adequate for the present. A partially associated solution model from the literature also proved inadequate However, with the aid of the extended liquidus and solidus data, a compositionally dependent model was developed to fit the solidus and liquidus isotherms [1] .

(B) In-Ga-P

Solidus and liquidus data were developed for the 800°C isotherm of $In_xGa_{1-x}P$ ternary system. The data extend over the region $0.49 < x < 0.90$, and have been developed by growing epitaxial layers of $In_xGa_{1-x}P$ on $In_yGa_{1-y}As$, InP, and GaAs substrates. The simple solution model was used to predict solidus and liquidus isotherms which fit the data. Compositionally dependent models were tried, but none proved satisfactory.

Several problems were responsible for the lack of extended data for this ternary system. In addition to the large lattice mismatch between the InP and GaP end-point binaries, the distribution coefficient of Ga in this ternary changes very rapidly with both the melt composition and the growth temperature. Another problem to be considered for this ternary is the lattice-pulling effect which has been previously observed and discussed for the epitaxial growth of $In_xGa_{1-x}P$ on GaAs substrates. In this effect, for a wide range of compositions of In-rich melts, solid compositions of lattice constants which varied little from that of GaAs were grown.

LPE techniques were devised to overcome these problems. Growth of lattice-matched $In_xGa_{1-x}P$ epitaxial layers on $In_yGa_{1-y}As$ substrates with the same lattice constant avoided the lattice-pulling phenomenon while providing extended solidus and liquidus data. Through use of the divided-melt technique, the lattice-pulling effect was observed and studied while at the same time extended solidus and liquidus data was acquired. The use of InP substrates for epitaxial growth of $In_xGa_{1-x}P$ extended the solidus and liquidus data farther still. Throughout all of these experiments, InP source wafers

were used to saturate the melts, thus allowing some comparison to and comment about the use of GaP source wafers for saturation as has been previously discussed in the literature [2] .

The work with the divided-melt technique has led to a new model to account for the so-called lattice-pulling effect. This model relies on dissolution of the GaAs substrate, followed by regrowth of In-Ga-As-P quaternary alloy [3] .

(C) In-As-P

Little effort has been previously invested in preparing $InAs_xP_{1-x}$ epitaxially. Previous work has yielded LPE layers in the range of $0.0 < x < 0.265$ on InP substrates at 600°C. The thermodynamic parameters derived from this limited data differ with those derived from the pseudobinary phase diagram calculations.

For the present proposal, extended solidus and liquidus data have been developed for the full range of composition for both 600°C and 700°C isotherms by growing epitaxial layers on both InP and InAs substrates. The step-grading technique was sometimes invoked, though single layers of large lattice mismatch were also grown. Furthermore, the simple solution model was found to be inadequate over the whole range of composition. Previous models might have been completed by interpolating between the end-point binaries, a method which turns out to produce acceptable fits to the data for this ternary. For the present proposal for 700°C the isotherms were finally constructed over the entire composition range using a piecewise analytical model. Compositionally dependent thermodynamic parameters were tried, but none proved satisfactory.

II. Epitaxial Layer Characterizations and Devices

Mn-doped $In_xGa_{1-x}As$

Mn-doped $In_xGa_{1-x}As$ crystals ($0 < x < 0.25$) have been grown by the LPE technique, and the doping characteristics and electrical properties of the layers have been studied by Hall measurement. The distribution coefficient of Mn has been found to depend on the substrate orientation. The acceptor energy level is about 77 meV and is comparable to that of Mn-doped GaAs. P-n junction diodes with high InAs compositions, grown using the step-grading technique, showed a diode factor of 2. Electron diffusion lengths greater that 3 μm have been measured in these Mn doped layers [4] .

(B) Cascade Solar Cell

Multiple-junction solar cells are made of two p-n junctions with different bandgaps connected together by a tunnel junction. The optimum bandgap combination is 1.2 eV and 1.8 eV. InGaAs is a suitable candidate for the low bandgap junction. The phase diagram work and the Mn-doping characteristics developed during the present program were helpful in the development of the cascade solar cell structure [5] .

(C) Photodector for the 1.8 μm - 2.0 μm Region

The development of both InGaAs and InAsP phase diagrams allowed us to build a photodetector for the 1.8 μm to 2.0 μm spectral range. This spectral region has until recently received little attention. The construction of the device includes step-graded layers of $InAs_xP_{1-x}$ grown on InP substrates. Lattice-matched to the final $InAs_xP_{1-x}$ layer is grown an epitaxial layer of $In_yGa_{1-y}As$ in which the p-n junction is created. Both Zn and Mn have been

used as p-type dopants. A photodetector of this construction has been developed with a peak quantum efficiency of 25% at 1.82 μm. The diffusion length of the active carrier at this wavelength has been calculated to be 0.48 μm. Spectral response measurements were made without the aid of any surface passivating window layers or the use of any anti-reflection coating [6].

III Development of Solid State Laboratories

As a result of this program, the Solid State Laboratories of the Department of Electrical Engineering at North Carolina State Uniersity has acquired some major assets. Two complete liquid phase epitaxy systems have been constructed. In addition, a set of three portable sorption pumps has been assembled. Major materials for an anaerobic glove box have been assembled. A Panametrics hygrometer has been acquired. Finally, complete computer algorithms of the regular solution technique for predicting the phase diagram isotherms of III-V ternary compounds have been developed.

IV Student Support

(i) C. Morrison, Ph.D. student (1979-1982). Expected date of completion: December, 1982. [7]

(ii) R. Fang, Post doctoral (1979).

Publications

The following papers have been prepared for publication as a result of this proposal:

(1) "Ga-In-As Solidus Isotherms Developed by the Step-Grading Technique", J. Appl. Physics, Oct. 1980, Vol. 51, pp. 5413-5418

(2) "Phase Diagram for the In-Ga-P Ternary System", accepted J. of Appl. Phys.

(3) "On the Lattice-Pulling Effect", to be submitted.

(4) "Electrical properties of Manganese Doped $Ga_{1-x}In_xAs$ Grown by Liquid Phase Epitaxy," Solid State Electronics, Vol. 23, pp. 839-844.

(5) "Growth and Characterization of Cascade Solar Cells," International Conference of GaAs and Related Compounds, Vienna, Sept. 1980.

(6) "Fabrication of an $In_xGa_{1-x}As$ Photodetector for the 1.8 μm - 2.0 μm Spectral Region," in preparation.

(7) "Liquid Phase Epitaxial Growth of In-Ga-As, In-Ga-P, and In-As-P," Ph.D thesis, Department of Electrical Engineering, North Carolina State University, in preparation.

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